Structural Characteristics of Double Network Gels with Extremely High Mechanical Strength

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ABSTRACT: The dynamic aspect of double network (DN) gels showing an extremely high mechanical strength has been investigated by dynamic light scattering (DLS) measurements. The DN gels are formed from highly cross-linked poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) as the first network and loosely cross-linked (or non-cross-linked) polyacrylamide (PAAm) as the second network. The results of DLS show that the presence of slow mode besides the gel mode (fast mode) enhances the strength of DN gels at the low cross-linking density of the second network. The dynamics of the slow mode cannot be explained in terms of reptational motion of the second component in the first network, but it is similar to the translational motion of PAAm polymers in a semidilute solution. A strong velocity dependence of the mechanical strength is observed at a shear rate close to the inverse of the relaxation time of the slow mode. These results suggest that large “voids” of the first network may exist, and PAAm polymers that exist in “voids” act as a “molecular crack stopper” in DN gels, keeping the crack from growing to a macroscopic level.

Introduction

Gel scientists have paid attention to hydrogels, which are made of swollen, cross-linked polymer networks and contain more than 90 vol % water. If hydrogels are functionalized with free chains on their surfaces,[1] these gels exhibit low surface friction and thus serve as attractive candidates as artificial replacements for damaged cartilage. Unfortunately, most of hydrogels made from either natural or synthetic sources suffer from lack of mechanical strength.

Recently, we have reported a novel method to overcome this problem by inducing a double network (DN) structure for various combinations of hydrophilic polymers.[2] These DN hydrogels, containing about 90% water, exhibit fracture strength as high as a few to several tens of megapascals[3−6] and show high wear resistance due to their extremely low coefficient of friction.

The DN gels are comprised of two independently cross-linked networks, and an optimal combination is found when the first network is a rigid polyelectrolyte and the second one is a flexible neutral polymer. We also found that the cross-linking density of the two networks and the molar ratio of the two polymers are two crucial parameters in improving the resistance against stress. A gel with highest strength is obtained when the first network is highly cross-linked and the second is slightly cross-linked or even without cross-linking. The DN gel becomes very strong in mechanical properties only when the molar ratio of the second network to the first network is in a range of several to a few decades. This is in strong contrast with the conventional IPN or semi-IPN hydrogels, which usually are equimolar in composition and therefore do not exhibit substantial improvement in mechanical strength.

As the highly cross-linked first network has a high Young’s modulus but is quite brittle on its own, we have assumed that the dramatically enhanced mechanical strength is due to an effective relaxation of stress by loosely cross-linked second networks which dissipates the fracture energy and prevents crack development. In this work, we concentrated our attention on the molecular dynamics of the second network by changing the cross-linking density of the second network while fixing the molar ratio between the two networks using the dynamic light scattering (DLS) technique. As a result of DLS, it is shown that the presence of a slow mode besides the “gel mode” (fast mode) correlates with the enhancement of the strength of DN gels at the low cross-linking density of second network. The origin of the slow mode and its role in the dramatic increase of the strength have been discussed.

Experimental Section

Materials. 2-Acrylamido-2-methylpropanesulfonic acid (AMPS) (Tokyo Kasei Co., Ltd.) was used as received. Acrylamide (AAm) (Junsei Chemical Co. Ltd.) was recrystallized from chloroform. *N*,*N*′-Methylenebis(acrylamide) (MBAA) (Tokyo Kasei Co., Ltd.) used as a cross-linking agent was also recrystallized from ethanol. 2-Oxoglutaric acid (Wako Pure Chemical Industries, Ltd.), which was used as an initiator, was used without purification.

Gel Preparation. The DN gels are referred to as P_1-x_1-y_1/P_2-x_2-y_2, where P_i, x_i, and y_i (i = 1, 2) are the abbreviated polymer name, the molar monomer concentration, and the cross-linker concentration in mol % with respect to the monomer, for the ith network, respectively. For example, the first network of the PAMPS-1-4/PAAm-2-0.1 DN gel was synthesized from an aqueous solution of 1 M AMPS containing 4 mol % cross-linking agent, MBAA, and 0.1 mol % initiator, 2-oxoglutaric acid, in a reaction cell containing a pair of glass

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plates with 2 mm spacing. This first network gel was then immersed in an aqueous solution of 2 M AAm, containing 0.1 mol % MBAA and 0.1 mol % 2-oxoglutaric acid, for 1 day until equilibrium was reached. The second network was subsequently synthesized in the presence of the first network. The gel thus prepared consists of two independent polymer networks entangled with each other.

Measurements. The compressive stress−strain measurements were performed on water-swollen gels using a tensile-compressive tester (Tensilon RTC-1310A, Orientec Co.). A cylindrical gel sample of 9 mm diameter and 4 mm thickness was set on the lower plate and compressed by the upper plate, which was connected to a load cell, at a strain rate of 10%/min. The strength of plate gels that resist slicing with a cutter (cutting breaking stress) was also measured on specimens of 20 mm length, 5 mm width, and 4 mm thickness. In this test, a technical apparatus with cutter of 0.05 mm thickness was used in the velocity range between 8.3×10^{-7} and 3.3×10^{-5} m/s.

Dynamic light scattering (DLS) experiments[7] were carried out on a static/dynamic compact goniometer (SLS/DLS-5000, ALV, Langen, Germany) at a fixed angle of 90°. A He−Ne laser with 22 mW (the wavelength in a vacuum; $\lambda = 632.8$ nm) was used as the incident beam. A typical measuring time was 30 s. The temperature of the sample was regulated at 25.0 °C within an error of ±0.1 °C. The characteristic decay time distribution function, $G(\Gamma)$, was obtained from the intensity−time correlation function, $g^{(2)}(\tau)$, with an inverse Laplace transform program (a constrained regularization program, CONTIN, provided by ALV).[8] The samples of DLS were prepared in narrow glass tubes with various diameters, considering their swelling ratios. After equilibrium swelling, they were transferred into the glass tubes of 10 mm inner diameter for DLS measurement.

As molecular weights of linear PAAm polymers ($y_2 = 0$) in DN gels could not be measured directly, the PAAm samples were polymerized in the presence of a linear PAMPS solution with the identical concentration of PAMPS single network (SN) gels from an aqueous solution of 2 M AAm and 0.1 mol % 2-oxoglutaric acid without MBAA. Molecular weights of PAAm samples were measured by a high-performance liquid chromatography (HPLC) system (LaChrom, Hitachi Co.), equipped with an L-7490 RI-detector and a KB-806M column (Shodex Co.). The commercial PAAms having regulated molecular weight were used as standards (PolyScience Co.). The measurement condition followed the previous research[9] with a slight modification: a buffer solution of 0.1 M Na_2SO_4 was used as an eluent at 40 °C, and flow rate was 0.4 mL/min.

Results and Discussion

As reported in a previous paper,[2] when the cross-linking density of the first network is kept at 4 mol % and only that of the second network is changed systematically from 0 to 1.0 mol %, all the PAMPS/PAAm DN gels show a similar elastic modulus of 0.3 MPa, a water content of 90 wt %, and a molar ratio of the second network to the first network of 20, regardless of the change in the cross-linking density of the second network. However, a dramatic change in the mechanical strength of DN gels is found, as shown in Figure 1. (For Figure 1, the area ratio will be discussed later in conjunction with Figure 4.) When the second network has a cross-linking density of 0 mol %, the highest fracture strength and strain are obtained. Incorporation of a second polymer with higher cross-linking density results in substantial lowering of the mechanical strength of the DN gel. Over the cross-linking density of 0.4 mol %, the fracture strength becomes a constant minimum. These results indicate that DN gels with a loosely cross-linked second network exhibit a higher mechanical strength.

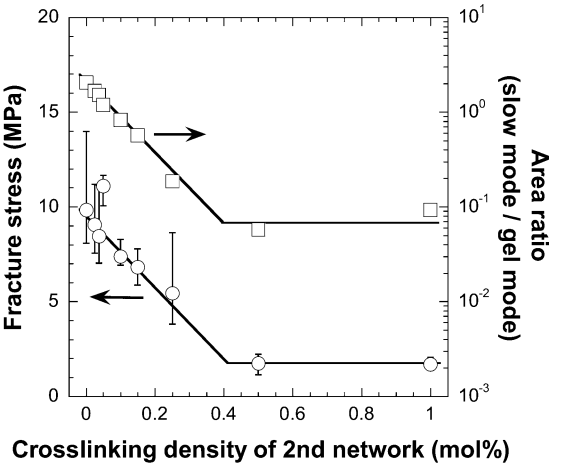

Figure 1. Effects of the cross-linking density of the second network (y_2) on fracture stress and on the area ratios of the slow mode to the "gel mode" obtained from Figure 4b,c. Sample: PAMPS-4-1/PAAm-2-y_2 DN gels (swelling degree, $Q_{\mathrm{swell}} = 10$).

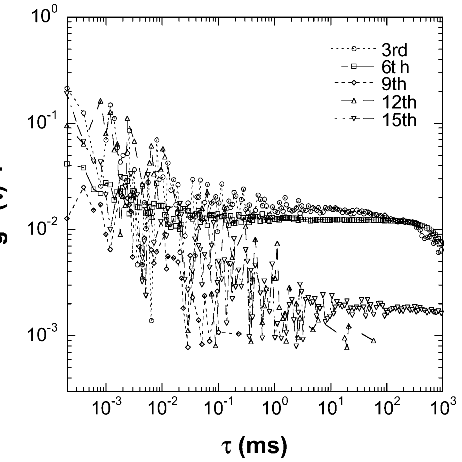

Figure 2. Intensity−time correlation function (CF), $g^{(2)}(\tau)$, of PAMPS single network (SN) gel. The measurement was carried out for 15 times at the same position. For clarity, only five data are shown.

PAMPS is a highly charged polyelectrolyte and strong repulsion between the immobilized polyions in water leads to a highly stretched conformation of the polymer chains. Although the intensity−time correlation functions (CF), $g^{(2)}(\tau)$s, for PAMPS single network (SN) gel were measured for 15 times at the same sample position, the CFs were very weak and not reproducible, as shown in Figure 2. This suggests that the first network, i.e., PAMPS network, behaves like an "immovable solid" with very rigid main chains in the range of the DLS measurement. Therefore, PAMPS network can be considered as an invisible background for DLS measurements of PAMPS/PAAm DN gels.

Figure 3 shows the effects of cross-linking density (y_2) on the CF and the characteristic decay time distribution function (DF) of the second network, i.e., PAAm SN gel. Around $y_2 = 0.2$ mol %, the behavior of DF changes. For $0 \le y_2 \le 0.2$ mol %, there are two modes, i.e., fast and slow modes, but there exists only one mode for $y_2 \ge 0.2$ mol %. The slow mode of DF in PAAm SN gel decreases and disappears by increasing y_2. Considering the time range of Γ^{-1} for respective mode, it is reasonable to deduce that the fast mode corresponds to the so-called "gel mode" and the slow mode to the translational mode of PAAm polymer. The variation of the slow

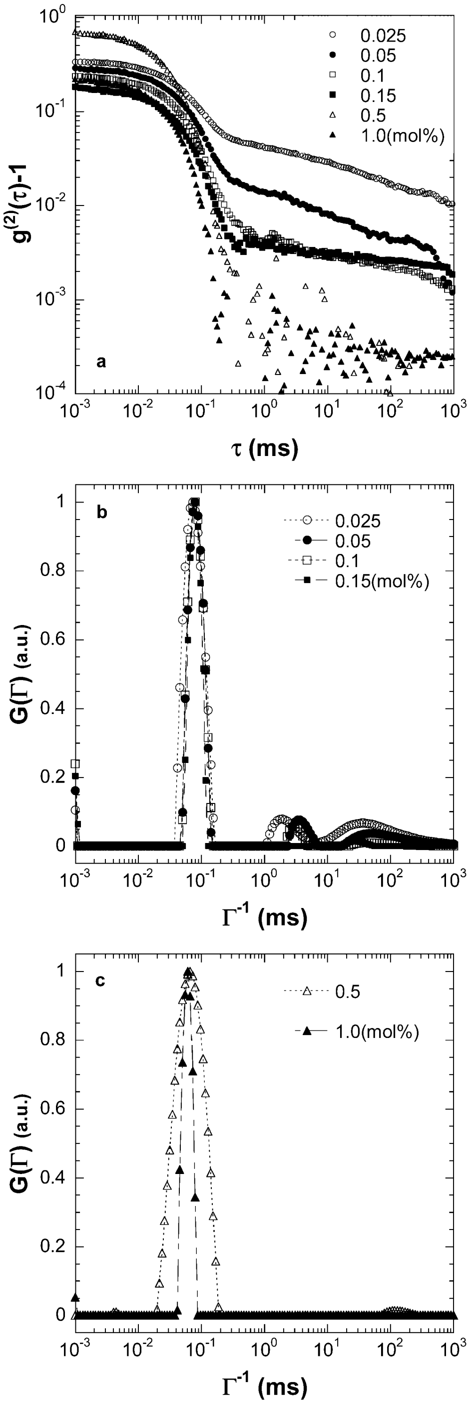

Figure 3. Effects of the cross-linking density (y_2) on (a) the CF and (b, c) the characteristic decay time distribution function (DF) in the PAAm SN gels for (b) $0 \leq y_2 \leq 0.2$ mol % and (c) $y_2 \geq 0.2$ mol %. The cross-linking densities (y_2, mol %) of PAAm SN gels are shown in the figures.

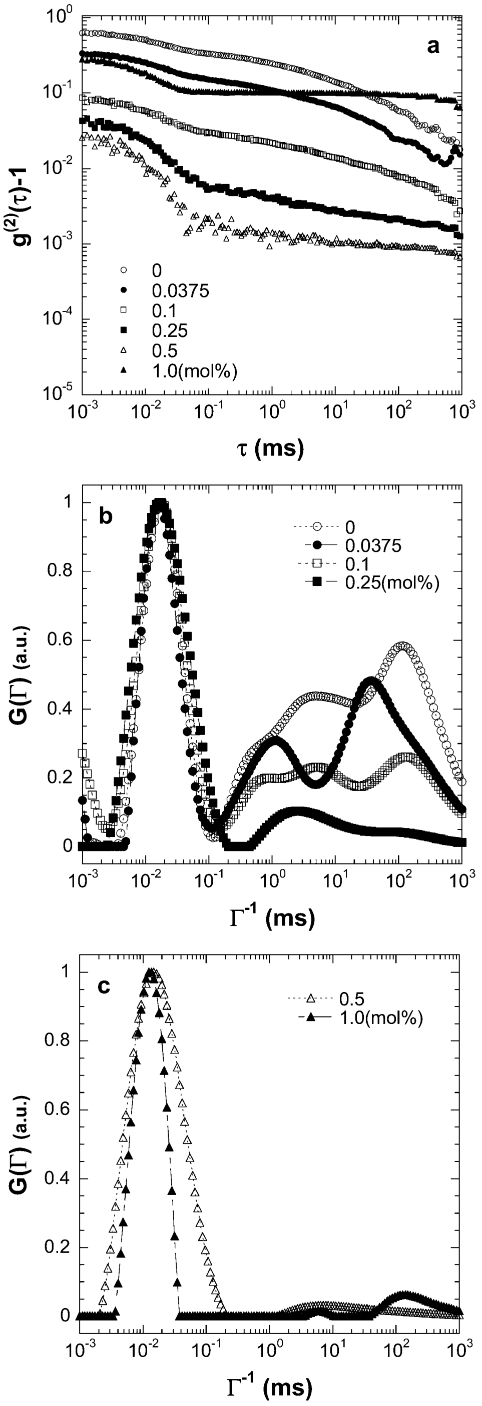

Figure 4. Second network cross-linking density (y_2) dependency of (a) the CF and (b, c) the DF in the PAMPS-4-1/PAAm-2-y_2 DN gels for (b) $0 \leq y_2 \leq 0.25$ mol % and (c) $y_2 \geq 0.5$ mol %. The second cross-linking densities (y_2, mol %) of PAMPS-4-1/PAAm-2-y_2 DN gels are shown in the figures.

mode with the increase in y_2 is thought to be related to the sol−gel transition of PAAm gel, as studied by Shibayama et al. for poly(*N*-isopropylacrylamide) gels and solutions.[10,11]

Figure 4 shows the effect of cross-linking density of second network (y_2) on CF and DF in the PAMPS/PAAm DN gels. As the first network PAMPS behaves as a background material in the time range of the DLS measurements, the DF of PAMPS/PAAm DN gels represents that of the second network PAAm. Similar to the DF behavior of PAAm SN gels, a slow relaxation has been observed besides the “gel mode” for $0 \leq y_2 \leq$ 0.25 mol %, but the slow relaxation disappears for $y_2 \geq$ 0.5 mol %. Compared with that of PAAm SN gels, the characteristic decay times of gel mode for PAMPS/PAAm DN gels ($\Gamma^{-1} \approx 10^{-2}$ ms) are much shorter than that for PAAm SN gels ($\Gamma^{-1} \approx 10^{-1}$ ms), indicating the trapping effect of highly cross-linked PAMPS (first network) to PAAm polymers in DN gels.

On the other hand, the slow mode in PAMPS/PAAm DN gels has a much wider relaxation distribution and a much large $G(\Gamma)$ value in comparison with that of PAAm SN gels. The area ratio of the slow mode to the “gel mode” has been calculated for DN gels, and its relationship with the cross-linking density of PAAm (second network) is shown in Figure 1. The result shows that that the cross-linking density dependence of the area ratio is very similar to that of mechanical strength. This suggests that the increased mechanical strength of DN gels correlates to the slow modes of $\Gamma^{-1} = 10^{-1}$–10^{3} ms in DN gels.

If we assume the slow mode of DN gel is diffusive, the diffusion coefficient of the slow mode in DN gels with a low y_2, D_{slow}, can be obtained from the result of DLS measurement as follows:

$$D_{\mathrm{slow}} = \Gamma/q^2 \tag{1}$$

where Γ is the characteristic decay rate and $q = 0.0187$ nm^{-1} is the scattering vector at 90°. From Figure 4b, D_{slow} is obtained as 2.9×10^{-11}–2.9×10^{-15} m^2/s for $\Gamma^{-1} = 10^{-1}$–10^{3} ms.

What is the origin of the slow mode in DN gels? If it is due to the reptation of PAAm (second component) in PAMPS network (first component), D_{rep} can be estimated from the reptation model[12]

$$D_{\mathrm{rep}} = {R_0}^2/\tau_{\mathrm{rep}} \tag{2}$$

$$\tau_{\mathrm{rep}} = N^3\tau_{\mathrm{blob}} \tag{3}$$

$$\tau_{\mathrm{blob}} = \eta\xi^3/k_{\mathrm{B}}T \tag{4}$$

where R_0 is the radius of PAAm polymer (cluster) with a Kuhn number N performing reptation in a swollen gel with a mesh size ξ. τ_{blob} is the relaxation time for a blob with the correlation length, ξ. η is the solvent viscosity at temperature T, and k_{B} is the Boltzmann constant. According to the result of HPLC measurement, the number-average molecular weight (M_{n}) and polydispersity index ($M_{\mathrm{w}}/M_{\mathrm{n}}$) of the linear PAAm polymer are 2.0×10^6 and 2.7, respectively. Approximately, the Kuhn number, N, is equal to the degree of polymerization in this work, so N is ca. 2.8×10^4 and $R_0 = aN^{3/5}$ (a = 2.5 Å) is ca. 120 nm. Supposing that the first network PAMPS is in a fully extended conformation, ξ is estimated to be 13 nm using the swelling degree, $Q_{\mathrm{swell}} = 45$.[13] From above results, $D_{\mathrm{rep}} \approx 10^{-21}$ m^2/s is found. This estimation shows that D_{rep} is much smaller than D_{slow} from that of DLS measurement, indicating that the slow mode of DN gel is not due to the reptation of PAAm in the PAMPS network.

How can the PAAm polymer with R_0 = 120 nm possibly exhibit a motion with a characteristic diffusion constant as high as a polymer cluster in free solution in PAMPS network with a small mesh size of 13 nm? A possible answer is due to the inhomogeneity of the PAMPS network. As studied by many gel scientists,[14−24] the inhomogeneity is an intrinsic property of polymer gel obtained from radical polymerization. Wu et al. pointed out that large “voids” are formed if the growing rate of polymer “clusters” is much higher than their relaxation rates (diffusion) and the voids between polymer “clusters” (microgels) are much lager than the mesh size between cross-linked chains inside the microgels.[20−22] Consequently, the dynamics of the slow mode in DN gels might result from a free motion of PAAm clusters in “voids” of PAMPS networks. The wide distribution of the slow mode in the DN gels with low y_2 is probably due to the partial entanglement of PAAm to PAMPS networks.

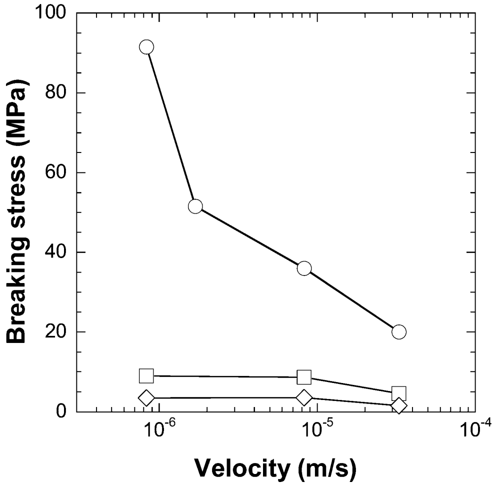

Figure 5. Cutting velocity dependency of breaking stress in the PAMPS-1-4/PAAm-1-0.1 DN gels (○), PAAm-1-1 SN gels (□), and PAMPS-1-8 SN gels (◇).

Table 1. $\tau_{\mathrm{slow}}\dot{\gamma}_{\mathrm{cut}}$ of PAMPS-1-4/PAAm-1-0.1 DN Gels with Change of Cutting Velocity

v_{cut} (m/s)	$\dot{\gamma}_{\mathrm{cut}}$ (s^{-1})[a]	$\tau_{\mathrm{slow}}\dot{\gamma}_{\mathrm{cut}}$[b]	breaking stress (MPa)
8.3×10^{-7}	6.9	0.35	91.5
1.7×10^{-6}	14	0.7	51.5
8.3×10^{-6}	69	3.5	36.0
3.3×10^{-5}	275	13.8	20.0

[a] $\dot{\gamma}_{\mathrm{cut}} = v_{\mathrm{cut}}/R_0$, R_0 = 120 nm. [b] τ_{slow} is 5.0×10^{-2} s at Γ^{-1} = 10 ms.

If the high mechanical strength of DN gel is due to the effective energy dissipation by the slow mode motion, the mechanical strength of a gel should be velocity-dependent when the measurement is performed at a shear rate near the inverse of the relaxation time, τ_{slow}, of the slow mode. Figure 5 shows that breaking stress changes with cutting velocity for PAMPS-1-4/PAAm-1-0.1 DN gels and PAMPS and PAAm SN gels. The breaking stresses of DN gels decrease with increasing cutting velocity at a range of 8.3×10^{-7}–3.3×10^{-5} m/s while PAMPS SN gel with a cross-linking density 4 mol % and PAAm SN gel with a cross-linking density 1 mol % show a much lower breaking stress with almost no velocity dependence. Supposing the slow mode is due to translational diffusion of polymer chain with a radius, R_0, we try to compare the relaxation time of the slow mode, τ_{slow}, with cutting strain rate, $\dot{\gamma}_{\mathrm{cut}}$, as follows:

$$\tau_{\mathrm{slow}}\dot{\gamma}_{\mathrm{cut}} \sim ({R_0}^2/D_{\mathrm{slow}})(v_{\mathrm{cut}}/R_0) \tag{5}$$

Here, v_{cut} is the cutting velocity. Table 1 shows the results by letting $D_{\mathrm{slow}} = 2.9 \times 10^{-13}$ m^2/s at $\Gamma^{-1} = 10$ ms and R_0 = 120 nm. As shown in Table 1, the breaking stress substantially decreases when the cutting velocity increases to a value of $\tau_{\mathrm{slow}}\dot{\gamma}_{\mathrm{cut}} > 1$. This result also suggests that the enhancement of mechanical stress of DN gel is associated with the relaxation of the slow mode.

Accordingly, we propose a structural model for PAMPS/PAAm DN gels showing a high mechanical strength. As shown in Figure 6, PAPMS networks (first component) are rigid and inhomogeneous, and large “voids” exist due to the specific radical polymerization mechanism. When PAAm are polymerized in the PAMPS network, some of them are interpenetrated in the PAMPS network and others are filled in the large “voids” of PAMPS gel,

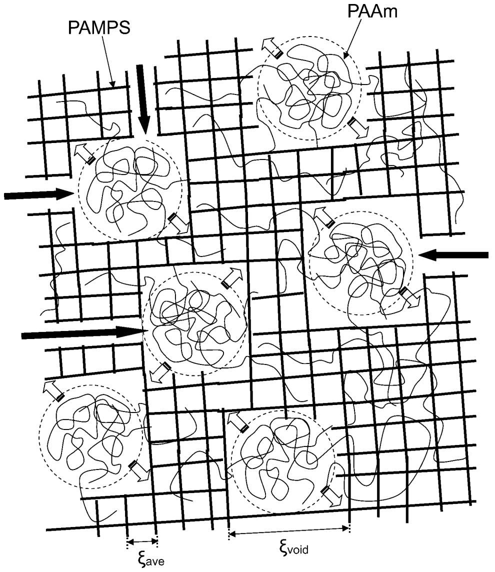

Figure 6. Structural model and mechanism to prevent crack development in PAMPS/PAAm DN gel. For simplicity, this schematic representation especially shows the case of DN gel in which the first PAMPS network is a rigid polyelectrolyte, and the second PAAm one is a flexible neutral polymer (cluster) without cross-linking, showing the highest fracture strength and strain. The mesh size of void, ξ_{void}, is much larger that average mesh size of PAMPS network, ξ_{ave} ($\xi_{void} \gg \xi_{ave}$).

partially entangled with the PAMPS network. The linear or loosely cross-linked PAAm in the "voids" effectively absorbs the crack energy either by viscous dissipation or by large deformation of the PAAm chains, preventing the crack growth to a macroscopic level. In other words, one possibility is that the increased mechanical strength of DN gels results from the effective relaxation of locally applied stress and dissipation of the crack energy through diffusive fluctuation of the PAAm polymer (cluster). The other is that the part of PAAm polymer entangled with PAMPS network can be an "anchor", and PAAm polymers with high molecular weight may be stretched very largely and ruptured during the fracture process, consuming the crack energy.[25]

Conclusion

The results of DLS show that the presence of slow mode besides the gel mode (fast mode) enhances the strength of DN gels at the low cross-linking density of second network.The dynamics of the slow mode is much faster than reptational motion of the second component in the first network, and it is close to translational motion of PAAm polymer (clusters) in semidilute solution. The strong velocity dependence of breaking stress of the gel in a velocity range comparable with the relaxation time of the slow mode suggests that the loosely cross-linked second network effectively dissipates the crack energy, keeping the crack from growing to a macroscopic level. An inhomogeneous structure model, which consists of PAMPS network with large "voids" and flexible and soft PAAm polymers, is proposed. The proposed structural model of DN gel shows that the "crack stop" occurs not in the polymer mesh size level (~ nm) but in larger spatial scale (size of voids), probably several hundred nanometers. The DN gel should be a good model system to investigate the inhomogeneous structure effect on the fracture strength of biomaterials such as articular cartilage, tendon, etc.

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